# Enhancement of Multiphoton Emission from Single Multichromophoric Molecules Using Plasmonic Nanostructures

Abstract of Master's Thesis, 2018

# Enhancement of Multiphoton Emission from Single Multichromophoric Molecules Using Plasmonic Nanostructures

Graduate School of Science and Technology, Kwansei Gakuin University

化学専攻, Masuo Laboratory, Yoshua Albert Darmawan

**[Introduction]** Previously, it was demonstrated that the multiphoton emission from single quantum dots (QDs) could be enhanced using localized surface plasmon resonance (LSPR) effect of plasmonic nanostructures[1]. Generally, QDs exhibit single-photon emission because exciton annihilation process occurs even when multiexciton are generated in a single QD. Near plasmonic nanostructures, QDs exhibit multiphoton emission due to the enhancement of the photon emission rate which prevents the exciton annihilation. Similarly, the multichromophoric molecule also exhibits single-photon emission due to efficient $S_1$-$S_1$ annihilation (SSA)[2]. In this work, the interaction between perylene-based multichromophoric molecules and plasmonic nanostructures was investigated. First, the emission behavior of two perylene-based multichromophoric molecules with different structure, tetra BP-N-PDIC and spiro F-B-PDI (Fig.1), was investigated. Then, influence of the plasmonic nanostructures on the emission behavior, particularly, the emission photon statistics, from single multichromophoric molecules were investigated.

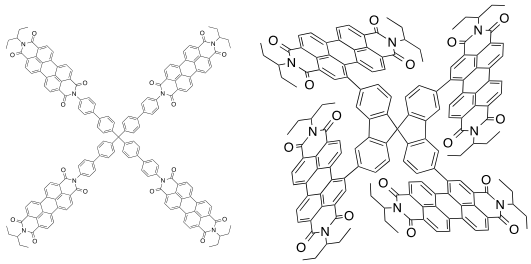

Fig. 1 Tetra BP-N-PDIC molecule (left) and spiro F-B-PDI (right)

**[Experiments]** The individual molecules were dispersed in PMMA 0.5 wt % in $CHCl_3$ and spin-coated onto a cleaned cover-slip. The emission behaviors of each immobilized molecule were investigated using a confocal microscope combined with 470 nm femtosecond laser excitation. The interaction between molecules and metal nanoparticles, silver nanoparticle (AgNP) and gold nanoparticle (AuNP), were observed by drop-casting the nanoparticles suspension onto the PMMA layer.

**[Results]** The emission behaviors of a single tetra BP-N-PDIC molecule without metal nanoparticles are shown in Fig.2 (a-c). From Fig.2 (b), it was confirmed that this molecule exhibited efficient single-photon emission due to efficient SSA process which indicated by $g^{(2)}(0) < 0.25$. The tetrahedral carbon core with biphenyl arms provides a good separation distance between the chromophores limiting the interaction between chromophores (Fig. 1). On the other hand, the spiro F-B-PDI molecule showed multiphoton emission and altered absorption and emission spectra due to delocalization of excitation caused by strong interchromophoric interaction. From these results it was concluded that the tetra BP-N-PDIC molecule is suitable for interaction with the plasmonic nanostructure.

The emission behaviors of a single tetra BP-N-PDIC molecule near AuNPs are shown in Fig. 2 (d-f). In Fig. 2 (d), it was shown that the fluorescence intensity was enhanced. Furthermore, this molecule also exhibited multiphoton emission and shortened fluorescence lifetime as shown in Fig. 2 (e, f) due to excitation rate enhancement and relaxation rate enhancement near AuNP. The excitation and relaxation rate enhancement of individual chromophores decreases the efficiency of SSA, which induce simultaneous photon emission from multiple chromophores. Consequently, by the decrease in the SSA efficiency, excitation rate enhancement, and radiative rate enhancement, the fluorescence intensity was enhanced near MNP. The fluorescence intensity enhancement can be observed in the first fluorescence intensity where the number of active chromophores is the highest.

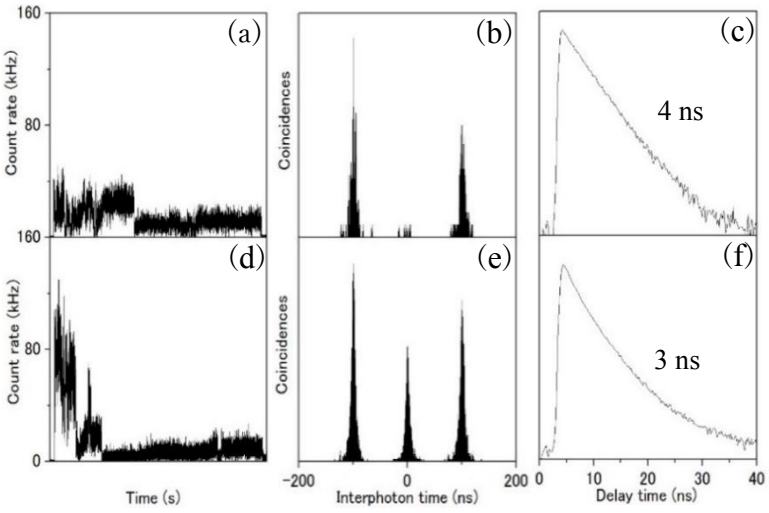


Fig. 2 Intensity traces (a, d), photon correlation histograms (b, e), decay curves (c, f) detected from molecule only (a, b, c), molecule near AuNPs (d, e, f)

**[Conclusion]** The plasmonic nanostructures modified the photophysical process of the individual chromophore, i.e., the plasmonic nanostructures decreased the SSA efficiency between chromophores in the multichromophoric system which resulted in the increase in simultaneous photon emission from chromophores in the multichromophoric molecule. These results indicate that the photon emission statistics, fluorescence lifetime, and fluorescence intensity from single multichromophoric organic molecule can be controlled using LSPR generated by plasmonic nanostructures.

**[Reference]**


1) H. Takata *et al, Nano Lett.* **2016**, *16*, 5770–5778.
2) S. Masuo *et al, J. Phys. Chem. B* **2004**, *108*, 16686–16696.
3) S. Bidault *et al, ACS Photonics* **2016**, *3*, 895–903.